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ULTIMATE DISPOSAL OF WASTE WATER. 1. A PHILOSOPHICAL VIEW. 2. ULTIMATE DISPOSAL OF WASTE WATER CONCENTRATES TO THE ENVIRONMENT

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ULTIMATE DISPOSAL OF WASTE WATER: A PHILOSOPHICAL VIEW

Robert B. Dean

The purpose of all pollution control activities, including ultimate disposal, is, of course, to avoid pollution. To some engineers and others responsible for the management of manufacturing, pollution control is an extra expense that people have started to get excited about, but, since they never worried about it before, maybe it will go away if we can wait out the present excitement. Actually, all activities produce waste, they always have, and they always will. Disposal of these wastes has always been a problem and one that requires the expenditure of money without the production of anything that can be sold for a profit. When the wastes from our activities are carried off in water, they used to be called *sewage*. However, sewage is a dirty word, so now we talk of wastewater. Actually, water itself, is rarely a waste but is frequently the carrier of other wastes. If these wastes interfere with the intended use of the water, they are by definition pollutants, and the water carrying the waste is polluted. If we are to avoid the unwanted effects of polluted water, we must remove the pollutants. The Federal Water Pollution Control Administration has, as its major assignment, the removal of pollutants from water. Since no agency and no government can single-handedly deal with all pollutants, one of our jobs is to find ways to reduce the cost of removing pollutants and make it easier for everyone to do his share to reduce pollution.

Unfortunately, removal of pollutants is only half the job. In an ideal world, every manufacturing process would include adequate waste disposal. However, for convenience, engineers break up complicated processes into manageable units. This is particularly true of chemical engineers, who, for a couple of generations, have been taught in terms of systems of unit operations. In each of these operations the product and the by-products pass on to the next step, and it has been all too easy to ignore what you don't want to think of, namely disposal of the by-products. Thus it is that the advanced waste treatment research program developed unit operations for the removal of the various pollutants in water and gave only nominal attention to the ultimate disposal of the wastes. It was not until 1967 that a formal program of ultimate disposal was established, and recognition was given to the fact that different wastes required different types of ultimate disposal.

It was axiomatic from the beginning that wastes which were removed from water could not be disposed of by putting them back into the sewer. A careful examination of the environment shows seven possibilities for disposal. These are, in order: outer space, atmosphere, freshwater, saltwater, land surface, underground, reuse.

Disposal in outer space is repeatedly mentioned and not always facetiously in this day of lunar exploration. Only a few moments' thought will be sufficient to show that this is by far the most expensive and least efficient method of ultimate disposal. The Apollo 11 shot expended 6 million lb. of fuel to put, among other things, less than 60 lb. of waste clothing on the moon, and the wastes are still there and may some day be objectionable. If we could shoot wastes into the sun, they would presumably be burned up, and even highly toxic radioactive wastes would be safe against the background of radioactivity in the sun. Even here it is hard to conceive of a waste that could not be taken care of at lower cost in some other way.

Whenever we consider the disposal of a waste to a location, we must consider whether additions of our waste pollute the local environment and interfere with the intended use of that environment. This is a chemical problem. For example, nitrogen in organic compounds excreted by animals will, if allowed to lie around, be converted into highly odoriferous and objectionable products of decay. By suitable treatment, these nitrogenous materials can be converted into less objectionable gases and vented to the atmosphere. It obviously makes a very big difference whether the nitrogen is converted into ox-

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ides, or is reduced to ammonia, or is released as nitrogen gas. In the first place, the oxides of nitrogen are known air pollutants responsible in part for smog conditions which threaten all our major centers of population. The release of substantial quantities of oxides of nitrogen from the treatment of wastewater would not be tolerated. Fortunately, none of the oxidative techniques for the destruction of waterborne wastes contributes significantly to nitrogen oxide in the atmosphere, although high temperature incineration can fix atmospheric nitrogen as oxides.

Ammonia in the form of household ammonia water has a strong pungent odor which many find objectionable. It is volatile and can be removed from water by aeration. Fortunately, again, the maximum concentrations of ammonia which are present in wastewaters are far below the level that is detectable by odor and even further below any toxic limits, so discharge of ammonia to the atmosphere appears to be safe. Ammonia discharged to the atmosphere will be adsorbed rapidly by plants, by moist soil, and by surface water as well as by rainfall. Discharge to the air over large bodies of water which already suffer from an excess of nutrients might, therefore, be objectionable, but in most areas the sole detectable effect would be a slight increase in the fertility of the land or the ocean.

The ideal form for the ultimate disposal of nitrogen is, of course, as nitrogen gas. This is not a difficult problem chemically and is even easier to do with the aid of microorganisms. Oxidation of wastes by conventional sewage treatment, if carried to completion, converts all of the nitrogen to nitrates. If the wastes are then supplied with food under anaerobic conditions, the nitrates are reduced almost quantitatively to nitrogen gas. It is inconceivable that any quantity of nitrogen gas so liberated to the atmosphere could be considered to be a pollutant.

The release of other elements to the atmosphere is not so easy. Carbonaceous compounds can, of course, be burned to produce carbon dioxide which may be accompanied by a small quantity of carbon monoxide. Recently, we have realized that discharges of carbon dioxide to the atmosphere may be pollutional in that it may change the temperature of the earth by interfering with solar radiation. Before we get excited about incineration of sewage sludges, it would be well to put this into perspective against the other sources of carbon dioxide in the atmosphere. Virtually all of the carbon present in municipal sewage is derived from vegetable and animal products which in turn derived their carbon from the atmosphere within the last couple of years. Return of this carbon to the atmosphere should therefore be acceptable, whereas the sudden conversion (on a geological scale) of large quantities of fossil fuel to carbon dioxide may be disastrous for the world as we know it today. Fortunately, carbon dioxide in the atmosphere comes to fairly rapid equilibrium with the ocean which represents a large, but not infinite, buffer system. It should also be pointed out that the most popular alternative to incineration of sludges is land spreading, and this also within a couple of years results in the conversion of almost all of the organic matter to carbon dioxide by microbial oxidation.

There are very few other substances that can safely be discharged to the atmosphere. Water vapor under most conditions is acceptable and does not pollute the atmosphere. However, excessive amounts of water vapor from cooling ponds and cooling towers could, under some conditions, cause objectionable fogs. Most other gases are highly objectionable, and their discharge to the atmosphere should be carefully controlled in the same way that the discharge of solids to the atmosphere is regulated in most large communities. A recent feature article in a leading journal devoted to pollution control opens with a picture of a large power station which has "high stacks for SO_2 dispersal." The station in question is located in a remote area so that the sulfur dioxide will be fairly dilute by the time it reaches the ground and is converted into calcium sulfate by the soil minerals. The same philosophy would not apply to sulfur dioxide dispersal from a heavily industrialized area with prevailing winds that carry the oxides of sulfur over a countryside that is lacking in natural limestone to neutralize the acids. Such is the situation in Sweden today. Recent studies have shown that the large quantities of sulfur oxides arising from industrialized Western Europe are coming down as rainfall in the granite catchment basins of southern Sweden and are producing acidities as low as *p*H 2.85. In this situation the building of high stacks is seen to be another example of the delusion that dilution is the solution to pollution.

The next possible place to put pollutants, and by far the most convenient for waterborne wastes, is to our freshwaters. Here the law and the philosophy of pollution control is clear. As a matter of national policy we do not condone the pollution of freshwaters which we consider to have other and more valuable uses. Therefore, the only fraction of wastewaters which we can safely discharge to surface waters is clean water itself, and even here we must guard against flooding, erosion, and possible thermal effects. The law books are full of statutes and cases regarding the mechanical effects of unwanted discharges, and we are beginning to pay the same sort of attention to the chemical and biological effects of discharges. But first I want to talk about the purely thermal effects.

Heat is as real a pollutant as brine or acid even though it is intangible and not regarded as a substance in the way that our alchemic ancestors used to regard caloric. Heat, in fact, is one of the few wastes that can be disposed of to the atmosphere without causing pollution. Heated air rises, and the heat is lost eventually by radi-

ation to outer space. Unfortunately, air does not have a very high heat capacity, and it costs a lot of money to cool by circulating air. It is, in most situations, much more economical to use water for cooling, and the cheapest way to dispose of the heated water is to return it to surface waters. The result is an increased temperature of the surface water. Warm water holds less oxygen than cold water, uses up what oxygen it has faster by biological action, and speeds up all biological processes. Unfortunately, all living things have an optimum temperature for growth and cannot tolerate for long times exposure to temperatures which are significantly higher than the optimum. Therefore, it is very easy to upset the ecological balance of nature by discharges of heat which might appear to be inconsequential to a chemical engineer. Many of us are familiar with the fact that trout live only in cold waters. A large power plant can easily discharge enough heat to destroy a famous trout stream. In a different situation this heat might be an advantage, for example, in very cold waters where an increase in temperature could improve the food supply.

The disposal of pollutants including heat in limited quantities to surface waters and potable underground waters is now subject to state and national regulations, and with few exceptions these waters are not acceptable places for the ultimate disposal of pollutants removed from water. On the other hand, there can be little objection to the return of sodium chloride to the ocean. The same is true of the other major ions of the ocean, including potassium, magnesium, calcium, sulfate, bicarbonate, and perhaps borate. If these salts are well mixed into the ocean, they will be completely undetectable against the natural background. Conversely, it is now apparent that certain toxic chemicals which are accumulated in the food chain, such as DDT and other persistent chlorinated hydrocarbons, and some toxic metals, such as mercury, should not be discharged in substantial quantities anywhere into the ocean.

Between the acceptability of sodium chloride and the unacceptability of mercury lies a large range of substances that are difficult to assess for suitability of disposal in the ocean. Biological nutrients form a particularly difficult class. In suitable quantities they may be highly desirable supplements to the ocean, increasing the world's food supply and thus contributing to the welfare of man. In large quantities they can cause objectionable side effects, such as algal blooms, and may lead to the disappearance of desirable species.

Sometimes the chain of cause and effect is very complicated. For example, it is common practice to treat municipal sludges by anaerobic digestion prior to discharge into the ocean. This treatment results in the liberation of substantial quantities of soluble amino acids from the solid matter. According to some recent work done by Professor Wheeler North and his students at Cal Tech, the sea urchin is able to absorb amino acids from solution and maintain its population in the absence of its natural food supply, the giant kelp. Normally, the sea urchin population and the giant kelp population are kept in a fair balance; however, if the sea urchin population is artificially supported, it is very difficult for the giant kelp to make a comeback after a portion of its range has been depleted. This is intentionally a complicated example that is still far from completely worked out. It is included to show the difficulty of deciding what is appropriate treatment for ultimate disposal.

In the case of ocean disposal, it is obvious that one should remove substances which float to the surface, not only rubber goods and plastics but also oil and grease, and one should also reduce pathogens to acceptable levels. Since the ocean is naturally aerobic except for a few holes, we probably should insist that discharges be aerobic and be sufficiently treated so that they will not cause large areas of anaerobic bottom.

Organic matter that has been derived from growing plants is usually rapidly degraded by microorganisms of the soil. Not only organic matter from recent crops but also substances from fossil plants that have been altered to petroleum are rapidly degraded. However, some synthetics including our old enemies, DDT and other chlorinated hydrocarbons, are only slowly decomposed in the soil. Inorganic substances similar to soil minerals, including compounds of calcium, aluminum, iron, and silicon, if properly mixed into the soil, are not problems. We have recently seen a field that has been built up by applications of calcium carbonate and fly ash until the plant roots can no longer reach the original soil surface, yet this field supports excellent crops of wheat and corn. Substances which should be avoided when applying waste to the soil include toxic metals, especially mercury, zinc, copper, arsenic, and selenium. It is also most important to guard against pollution of groundwater. Fortunately, the soil is an excellent adsorbent for most soluble pollutants. Notable exceptions are the anions which form very soluble salts, in particular chlorides and nitrates which can seriously pollute groundwaters.

In general, we know less of what lies underground and what happens to it than we know about the oceans. We don't know what will happen when large amounts of liquid are pumped underground in most cases, but we do know that in some cases the results will be regrettable. Disposal of solids underground by burial or storage in vaults is effective and acceptable, but unfortunately is very expensive. The high toxicity of radioactive wastes may justify the costs of underground burial, but it is doubtful whether deep burial will be appropriate for other solid wastes. Of course, landfill and above ground burial, including even the creation of artificial mountains, are seriously considered for municipal solid wastes.

The seventh and last possibility for ultimate disposal is reuse and return of substances to the bioindustrial cycle. Philosophically, this is the most attractive be-

cause the wastes by definition cease to be wastes when they are reusable. It is obvious that this earth contains a limited though frequently large supply of raw materials, and eventually these will have to be reused. It is interesting that water itself is the substance that has been reused in largest quantities by man, not only through the evaporation-precipitation cycle, but also by direct discharge to surface waters and use of these waters by other communities downstream.

The classical example of reuse of wastes is the meat packing industry. In the city of York in England, there is an interesting narrow little street with a central gutter called the Shambles. If you look this word up in the dictionary, you will find it means a place where meat is cut up. In the old days meat was butchered in this street and the offal (the off-fall from the tables) was thrown into this gutter. Eventually, the nuisance got so great that the butchers were driven out of town; no doubt they complained bitterly of economic loss just because people were worried about a little rotting meat. Later, the meat packers found that there was money to be made in their offal, and eventually they were able to boast that they used every part of the hog except the squeal.

It would be nice if all our waste problems were as easily solved. Unfortunately, reuse of wastes is expensive and is rarely a profit making operation. For example, in Chicago they estimate that it costs them $60 a ton to dry sludge which is then sold for agricultural purposes at $14 a ton. They obviously aren't making any money doing it this way, but that $14 is certainly better than paying someone to haul away the sludge. Most cases of reuse of wastes fall into this category.

The fundamental difficulty with reusing the wastes carried in sewage is their extremely high dilution. There is a law of thermodynamics which states that work required to remove a substance from solution increases as the logarithm of the dilution. Against this must be set the scale factor of treating wastes in large quantities. However, for wastes that are not amenable to conventional treatment, and here I refer particularly to industrial wastes, it is frequently most economical to remove them at the point where they are most concentrated. In other words, if you have a difficult waste problem, it may be best to isolate the components rather than mix them all together and then try to treat the mixture at high dilution.

At the present time the only component of wastewater which may be recovered and sold as a profit is the water itself. The organic content that is captured as sludge certainly has value but probably not sufficient to pay the costs of its removal. None of the salts present in wastewater are concentrated enough to justify a second look were we concerned only with an economic source. However, when we look at the problem from a pollution control point of view, there may be a number of substances which can be recovered to help pay part of the costs of treatment.

In conclusion, I want to repeat that there is no universal solution to the ultimate disposal problem. Each site and each substance must be examined specifically, and great care must be taken to insure that control of one sort of pollution does not produce a worse pollution problem elsewhere.

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Ultimate Disposal of Waste Water Concentrates to the Environment

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Advanced treatment of waste water is basically the separation of a valuable product—water—from its pollutants. The residue of substances which remains normally has no positive economic value, and must be degraded or disposed of (Weinberger, Stephan, and Middleton, 1966). In this respect, waste treatment is similar to other industrial processing: separating the wheat from the chaff, copper from its gangue, or wood pulp from lignin. These low value residues, like those from waste water treatment, are usually an economic liability and may become a pollutant. It is the assignment of the Ultimate Disposal Research Activity of the Federal Water Pollution Control Administration to devise methods for treating these residues so that they will not pollute the environment.

In this context, a pollutant is defined as a substance which interferes with the intended use of the water, air, or land surface. Since intended uses often conflict, society must decide on the best intended use. In the U.S., we are deciding that neither water nor air should be used for disposal of noxious substances. However, we still approve of controlled burial for unwanted organic matter and use of the atmosphere for carbon dioxide disposal. There is also no objection to putting clean water back into the river, and by corollary, there should be no objection to returning salt to the ocean.

A prime requisite of any disposal procedure is that a pollutant from one medium be prevented from causing pollution elsewhere. For example, incineration of sewage sludge requires control of particulate matter from the incinerator stacks. Wet scrubbers can effectively remove the fly ash from stack gases, but the water-ash slurry produced also requires further treatment before disposal. Although this seems to be an endless circle, each step of treatment does reduce considerably the quantity to be treated.

There are only three places where it is practical to dispose of polluting substances after they have been rendered innocuous: air, land, or the oceans. Surface fresh waters are not available for disposal. No substances except water itself can be disposed of in large quantities into fresh water without causing a pollution problem of some sort. The ocean has long been used for the ultimate disposal of human wastes, and the first man-made pollutant to attract attention in the ocean was fecal material. Removal of sewage solids by primary treatment deals with the obvious problems, and is often the only treatment given by seacoast towns today. However, warning signs are appearing. There is some evidence that the ocean's assimilative capacity is not infinitely large, and that the effluents from some ocean outfalls are not rapidly dispersed. To avoid pollution, these wastes must be treated to remove any material which will float to the surface. They must be placed far enough from shore and mixed with enough sea water to ensure adequate dilution. Disinfection may also be needed, especially if discharges are close to bathing beaches and beds of edible shellfish.

Brooks (1960) has discussed the design of ocean outfalls for dispersion of dilute wastes that are lighter than sea water. Many communities load heavy sludge on barges and dump it at sea where, hopefully, it sinks to the

bottom. Fortunately, most toxic heavy metals present are converted to insoluble precipitates that settle to the bottom. Thus, they have a low rate of dispersion in the sea. Sea water also has a high buffer capacity and can neutralize large quantities of acids or bases.

Harmful or helpful

Disposal at or near the shoreline has the effect of increasing the fertility of offshore waters. The result may be beneficial, as in the case of an improved environment for shellfish breeding and survival, or harmful, as in the case of unwanted blooms of algae and microscopic organisms. In either case, not enough is known yet about the ecological effects of ocean waste disposal. One danger is that commerical fish catches may be the last link in a food chain that concentrates pesticides from waste waters to toxic levels. On the other hand, removal or neutralization of toxic substances could make possible the use of nutrient values of wastes to increase the productivity of the oceans.

Long distance transport of sludges and concentrates by pipeline was suggested by Wirtz in 1956. Relative costs of commercial carriers have been studied by Koenig (1968), who showed that pipelines are not the most economical method of transporting less than 10,000 gallons per day. Trucks are more economical than rail for hauls of less than 50 miles.

Solid materials may be disposed of on land, either as concentrated fill that is buried, or by dispersion on the surface. In either case, dissolved salts or toxic materials may pollute the ground water. Some states already prohibit the discharge of salt brines to unlined pits or dry watercourses. When solids are used for landfill, it is important that they be solid and capable of bearing a load. Organic sludges that decompose slowly cannot be used as fill under buildings, or even playgrounds, if the area is to remain level. Seepage from landfills pollutes surface and ground water (Weaver, 1961).

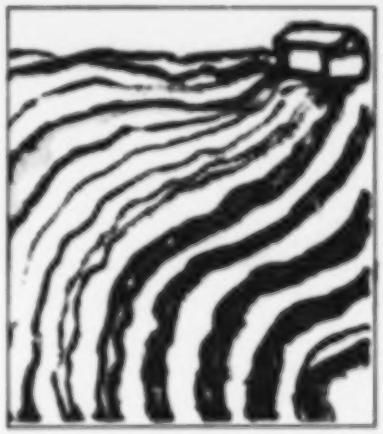
The cheapest, and oldest, method of sewage disposal is spreading of the liquid sludge on land (Kershaw and Wood, 1966). Odor problems and seepage to streams resulting from uncontrolled use of the technique have made spreading unpopular. Nevertheless, the method is still under study, since most soils have a considerable capacity for dewatering and oxidizing organic matter.

Land spreading of soluble organic salts or toxic material is, of course, undesirable. Farmers in some countries abroad use human wastes, without dilution, as a soil nutrient. However, the nitrogen, phosphorus, and potassium content of sludge is much lower than synthetic fertilizers, and the many U.S. attempts to market dried sludge as a fertilizer have been generally unsuccessful (MacLaren, 1961). The organic content of sludge is useful in improving the quality of sandy soils, although market value in this application hasn't been assessed realistically.

Market for sludge

Thus, the use of land surfaces as low cost dewatering and oxidizing systems has some promise. In many areas, farmers compete for available wet sludge to spread on their fields, indicating the possibility of developing some market value. In a typical operation, sludge is sprayed from a tank truck. If the soil is too wet to bear the weight of a truck, a high pressure hose and sprinkler may be used to bring sludge from the roadside. Soils can oxidize and destroy large quantities of sludge each year, provided they are kept well aerated. However, heavy metals in some sludges have caused loss of fertility after many years (Rohde, 1962).

Some form of digestion or stabilization is required before sludge can be applied to the land. For sale on the retail market, sludge is dried and heat-sterilized. Air-dried sludges are given away to farmers and greenskeepers all over the country. Anaerobically digested sludge is spread wet in many areas. A trend toward aerobically stabilized or digested sludge has been noted, particularly for smaller treatment plants. Aerobically stabilized sludge has fewer nutrients in the supernatant liquor and is more stable than conventional anaerobically digested sludge (Irgens and Halvorson, 1965). Some states prohibit the application of



unsterilized sludges to root or leaf crops.

A pipeline has been proposed to transport sludge to low quality land in Cook County and ultimately to land some 67 miles distant(Dalton et al., 1968). Morgantown, W. Va., has a grant to pipe sludges five miles to a strip mine spoil area to reclaim the soil. In both cases, local opposition to dumping of sewage "in our backyard" has developed. Proper communication is obviously important. Two plants near Pittsburgh, only 70 miles from Morgantown, are distributing wet sludge to farm land and finding it highly acceptable to the farmers (Wolfel, 1967).

Soluble waste such as salt solutions can be pumped into deep disposal wells —if the subsurface geology is suitable. This method is used widely for the subsurface return of oilfield brines. One drawback to the technique is that the pores of the underground aquifers can be clogged by solids suspended in the liquid. If underground rock formations can be fractured to open up bedding planes, suspended solids are less of a problem (Warner, 1965). Disposal into underground rivers in limestone formations is also practiced. Pollution of ground water is a concern for both shallow and deep wells, and earthquakes have also been attributed to underground injection of wastes (Healy et al., 1968).

Mined cavities, such as those used for underground storage of fuel gas, are more expensive than other means of ultimate disposal. They are more suitable, however, for disposal of radioactive wastes which require continuous monitoring.

Any logical approach to the problems of ultimate disposal must really begin with the chemistry of the pollutants. Fortunately, fewer than half of

the elements are common enough to be encountered in the search for solutions to disposal problems. In fact, only 29 of the elements constitute over 99% of the ultimate disposal problems. (Disposal of radioactive isotopes will not be included in this analysis. Their use and disposal are subject to strict Atomic Energy Commission control.)

The major problem facing municipal sewage treatment plants in the disposal of organic matter is not the carbon compounds themselves, but the associated water. A 5% primary sludge contains nearly 20 times as much water as all other matter. Obviously, it is not economical to use fuel to dry sludge beyond the point where it will support its own combustion. Sedimentation and filtration are two common methods of dewatering.

Oxidation by combustion is one method of ultimate disposal of organic matter which also provides heat that can be used to dewater sludge. Combustion of one pound of dry sludge may produce only enough heat to evaporate two pounds of water, whereas a greasy or oily sludge will be able to evaporate more than three pounds. In addition, the design of an incinerator has a large influence on the percent of water which can be evaporated without using supplementary fuel (Sebastian and Cardinal, 1968).

Fuel value

The fuel value of dry sludge is comparable to that of low grade coal (Owen, 1957), and can be measured accurately in a bomb calorimeter. With ordinary sludges, fuel value can be estimated from the percent volatile solids. However, because of the uncertain quantities of bound water in hydrous oxides, it is not safe to use this method to estimate the fuel value of sludges that are high in ash.

Various pretreatments of sludge are used to reduce the cost of drying. Anaerobic digestion, for example, reduces the quantity of sludge which must be handled. Digestion may also make the sludge somewhat easier to filter. A properly operating anaerobic digester reduces the filterable solids by up to 50%, fermenting them to methane and carbon dioxide and producing a supernatant liquor rich in nutrients and BOD (Barth, Mulbarger, et al., 1966). The methane can be burned to heat the digester or, in large plants, to generate power. In either case, it is oxidized to CO_2 and water vapor. The supernatant liquor is ordinarily returned to the plant where it increases the oxygen requirements and raises the levels of nutrient salts. The supernatant liquor is by far the most polluted stream in ordinary municipal sewerage systems.

The filterability of sludge can be improved greatly by the Porteous system of pressure-cooking at 370° F. The method was developed in England where it has since been abandoned at some plants (Evans and Roberts, 1947). A new heat treatment plant has been built recently in Switzerland (Lascoud, 1965). Pressure-cooking the sludge hydrolyzes the slimy substances that make filtration difficult, and also destroys living cells and spores; however, it liberates soluble nutrients and BOD to the supernatant liquor. Ten to 20% of the BOD and 60-80% of nitrogen is returned in the soluble fraction. In this respect, the supernatant liquor from cooking puts a greater load on the biological plant than a digester which, at least, coverts some of the soluble BOD to methane.

The Zimmerman wet oxidation process involves cooking the sludge in the presence of dissolved air (Teletzke, 1964). A high temperature version of this process, which operates just below the critical temperature of water, produces a sterile inert sludge, aldehydes, acids, and CO_2 from oxidation of the organic substances, and solubilized nitrogenous compounds. Lime may be added to retain the phosphates in the solids. The low temperature process products a sterile sludge cake that is high in organic matter, but can be filtered easily. The supernatant liquor is rich in amino acids and plant nutrients (Teletzke, Gitchel, et al., 1967). Like anaerobic digestion, heat treatment produces a strongly polluted stream which is difficult to treat in a biological plant.

Sludge stabilization

Aerobic digestion stabilizes solids against subsequent putrefaction and retains most of the nutrients and BOD in the insoluble fraction. It may produce a high level of nitrates in the supernatant liquor. There are small reductions in total BOD and nitrogen and no useful increase in filterability. Aerobic digestion, therefore, has little value as a pretreatment to filtration and incineration. Its principal use is stabilizing sludges for land spreading.

Organic matter applied to the soil is oxidized by the soil microorganisms to produce CO_2 and humus. Phosphates and ammonia are adsorbed on soil minerals and utilized by the crops. There may be some denitrification of soluble nitrates. Pathogenic organisms in raw sludge must be controlled by some form of treatment. Digestion—either aerobic or anaerobic—commonly is considered sufficient because the sludge should be held long enough in an unfavorable environment for pathogens to be killed. Heat treatment is ideal, but expensive, and chlorination of sludges is not practical. Lime treatment might be effective; most pathogens are destroyed above pH 12.

Phosphorus, perhaps the major uncontrolled pollutant in waste water, (Sawyer, 1965) occurs in at least three forms in raw sewage: orthophosphate, condensed phosphate, and organic phosphorus. Of these, the orthophosphate form is the primary nutrient for algal growth in surface waters. Present treatment methods remove only a fraction of the phosphate load as organic sludges. Biological treatment hydrolyzes about 90% of the total phosphate to orthophosphate in secondary effluents (Hurwitz, 1965; Neale, 1964).

Under certain conditions which are still not understood, activated sludges accumulate a large fraction of the phosphate present in waste water (Vacker, Connell, et al., 1967). Studies are under way to maximize this process since it could become a low cost way to remove phosphates. The phosphate accumulated by active sludge can easily be lost by relatively short anaerobic periods, and a large fraction of the phosphates is redissolved in digester supernatants (Shapiro, Levin, et al., 1967). If returned to the head of the plant, this supernatant adds to the phosphate load to be handled. In-

cineration of sludge retains phosphates in the ash. When organic sludges are spread on the land, the phosphate is adsorbed by the soil minerals and will serve as a nutrient for crops. However, erosion of phosphate-rich soil brings phosphates into surface waters where they can serve as algal nutrients.

A number of polyvalent cations are available which can precipitate orthophosphates from secondary effluents. Cheapest of these is calcium, in the form of lime. The calcium precipitate which forms is properly called hydroxyapatite, $Ca_5OH(PO_4)_3$, the same mineral that forms bones and teeth. [This mineral is often mistakenly referred to and calculated as tricalcium phosphate, $Ca_3(PO_4)_2$, which does not form in aqueous systems.] Phosphate minerals or rock phosphate are predominantly hydroxyapatite with substantial quantities of the isomorphous fluorapatite. Rock phosphate analyses are referred to in percent bone phosphate of lime (b.p.l.) which has the arbitrary formula of tricalcium phosphate (Van Wazer, 1958).

Speed up precipitation

Crystallization of phosphates from waste waters, normally supersaturated with apatite, even at a slightly alkaline pH, proceeds so slowly that weeks or even months would be required for precipitation of appreciable quantities of phosphates. One convenient way to speed up the precipitation is to raise the pH by adding hydrated lime. For example, the phosphate removal treatment at South Lake Tahoe (Slechta and Culp, 1967) adds 600 mg./l. of lime to the secondary effluent. At the alkaline conditions which result, a pH greater than 11, calcium carbonate and magnesium hydroxide precipitation proceeds via the same mechanisms that occur in cold lime softening of hard water. The gelatinous magnesium hydroxide precipitate aids in clarification and increases the removal of phosphates. One danger is that if the effluent is neutralized in the absence of a clarifying agent, some of the colloidal apatite crystals which remain in suspension may redissolve.

Lime-treated waste water sludges contain, in addition to apatite, calcium carbonate, magnesium hydroxide, and organic matter. Carbon dioxide can leach out the magnesium at pH 9.5, the pH of minimum solubility of calcium in the presence of carbonate (Eidsness and Black, 1957). The sludge may be calcined to convert the carbon-

ate to oxide, which can be slaked to calcium hydroxide for reuse. The apatite is unchanged during the calcining, and the magnesium oxide ordinarily does not slake, or hydrate, and remains with the inert fraction.

The major savings in lime sludge reuse comes in the reduction of ultimate disposal problems, since the lime sludges accumulate rapidly and are difficult to dispose of. Sale of the recovered material as low grade lime may be possible in some areas, but probably not at a profit. Recovered lime costs nearly as much as commercial lime, and the only savings on chemicals would be in the freight charges.

The natural hardness of water determines the actual extent to which lime reuse is possible. In hard water areas, lime treatment softens the water, and the excess lime that is produced complicates the ultimate disposal problem. In soft water areas, the situation is reversed, and the phosphates remove lime from the waste water. In this case, the recycled lime can build up an apatite level comparable to low grade rock phosphate, and may have some market value.

At the South Lake Tahoe plant, the lime is recycled about three times. At this point, the phosphates and inert substances reach a level where, lacking a local market for the phosphate, the waste must be dumped. Fortunately, the phosphate in the ash is insoluble and will not leach out into water percolating through the dump.

At approximately neutral pH, aluminum hydroxide can also be used to adsorb and precipitate phosphates. Under suitable adjustment of alkalinity, the hydroxide can be formed from either alum or sodium aluminate (Rohlich, 1963, 1954). The aluminum-phosphate complex involved is not known, but a polymeric form is likely. At any rate, a formula ratio of $Al(OH)_3AlPO_4$ is necessary for high removal efficiency (Henriksen, 1963).

Aluminate ions

At high pH, aluminum hydroxide redissolves to form aluminate ions. Phosphate ions, formed by the dissolution of some of the aluminum phosphate at high pH, can be precipitated as apatite by calcium (Lea, Rohlich, et al., 1954). Optimum conditions for aluminate recovery are under investigation at FWPCA laboratories in Cincinnati. For example, the addition of lime should be feasible for supplying a major part of the alkali needed. Neutralization of the alkaline aluminates might then provide the aluminum hydroxide for further treatment. Bicarbonate acidity may be sufficient for the neutralization, but in some cases more acid may be needed. Both aluminum and acid might be supplied as alum if some of the aluminum is lost with the calcium phosphate.

One promising source of aluminum hydroxide for phosphate removal is water treatment plant sludges. Aluminate is also available as a waste product from the anodic treatment of aluminum metal. Aluminum hydroxide is, of course, also soluble in acids, and some alum has been recovered this way from water treatment sludges (Roberts and Roddy, 1960). Since acids also dissolve phosphates, there is no practical way to separate phosphates from metal ions at low pH.

Aluminum hydroxide is very difficult to dewater, and disposal of aluminum hydroxide sludges presents a difficult problem. Surface spreading on land is not desirable because even small quantities of aluminum hydroxide clog the

soil, making it unfit for agriculture. Organic-rich sludges cannot be converted to aluminate because humic acids will dissolve. One successful, though expensive, method is to freeze the sludge (Doe, Benn, et al., 1965), which removes the water and yields an alumina that filters as easily as sand. Aluminum hydroxide with adsorbed phosphates apparently is not dissolved in anaerobic digesters, according to recent studies by Barth and Ettinger (1967). Incineration of the sludge should produce insoluble aluminum phosphates in the ash.

Iron salts also hydrolyze to gelatinous hydroxides which adsorb phosphates. Ferric phosphate is reduced in anaerobic digesters to insoluble ferrous phosphate (Thomas, 1965). If sulfides are present, the less soluble ferrous sulfide precipitates, liberating the phosphate. Ferric hydroxide, or the oxide after incineration, can be redissolved in acid but this also dissolves any phosphates. The Guggenheim process for chemical treatment of sewage with ferric sulfate, followed by incineration and recovery of ferric oxide by solution in sulfuric acid (Gleason and Loonan, 1933), was unsuccessful because phosphates accumulated with the iron. Unlike aluminum, it is not possible to dissolve ferric hydroxide at high pH. Iron salts may be useful for removing phosphates where low cost waste streams containing iron are available, such as acid mine wastes or pickling liquors. Leaching by ground water would probably not liberate phosphates from incinerated sludge containing iron phosphates.

Many other polyvalent metals can precipitate phosphates and some may be recovered by redissolving the precipitate at high or low pH. None of these metals is as cheap as lime, alum, or iron, and high recoveries would be necessary to justify the use of any other metal to precipitate phosphate.

Nitrogen compounds, like phosphates, are a serious pollutant in municipal waste waters and can stimulate the growth of algae to nuisance conditions. Some algae are nitrogen fixing, also converting atmospheric nitrogen to organic nitrogen which then enters the nitrogen cycle.

Nitrifying bacteria

Organic nitrogen compounds can be hydrolyzed to ammonia by microorganisms under aerobic or anaerobic conditions. Extended aerobic treatment develops nitrifying bacteria which convert ammonia, first to nitrites, and then to nitrates. High-rate biological treatment usually leaves most of the nitrogen in the form of ammonia. Extended aeration converts nearly all of the ammonia to nitrates (Barth, Mulbarger, et al., 1966).

Most nitrogen in waste water is in the form of either ammonia or ammonium ion at a typical concentration of about 15 mg./l. as nitrogen (Neale, 1964). If the waste water is to be treated for reuse, its ammonia content must be brought below 1 mg./l. The ammonia can be converted to gaseous nitrogen by chlorination, but such treatment requires 10 mg. of chlorine per mg. of ammonia nitrogen (McKee and Brokaw, et al., 1960). Such heavy chlorination would cost between five and ten cents per thousand gallons of water treated.

Air stripping

Ammonia is present almost entirely as ammonium ions at the alkalinity of normal secondary effluents, but above pH 10 it is mostly present as a dissolved gas. If the pH is run high enough at some stage of the treatment process—for example, by lime addition to remove phosphates—large cooling towers can be used to air strip the gaseous nitrogen. During aeration, the equilibrium is strongly in favor of the water phase, and about 300 cubic feet of air are required per gallon of water treated. The cost of air stripping is usually under two cents per thousand gallons (Slechta and Culp, 1967).

The large volumes of air necessary to remove ammonia make a preconcentration step desirable. Some zeolite minerals selectively adsorb ammonium ions in preference to sodium, calcium, and magnesium ions (Mercer et al., 1968). Battelle-Northwest is currently investigating natural zeolite for adsorption of ammonium ions from waste waters. Regeneration by lime and aeration of a few percent of the total volume to remove ammonia appear feasible. Ammonia levels in air from stripping towers will be extremely low (micrograms per liter), about comparable to nitrate nitrogen from electrical discharges in the atmosphere. Ammonia in the air is eventually adsorbed by soils and surface waters.

Ammonium ions applied to soils are adsorbed by soil minerals such as natural zeolites and clay, and are available to growing plants. Excess ammonia is converted by soil bacteria to nitrates by the same route that exists

in extended aeration. Nitrate ions are also utilized by growing plants but are not adsorbed on soil minerals. Excess nitrates, when leached out of soils, produce nitrates in ground water or crystals of saltpeter in caves and cellars.

The Public Health Service limit for nitrates in drinking water was set at 10 mg./l. as nitrogen in 1967. Higher levels are toxic to infants, causing methemoglobinemia, or "blue babies," although children and adults can handle large quantities of nitrates without difficulty.

As algal nutrients, nitrates in surface waters are not significantly different from ammonia on a nitrogen basis (Fleigg and Reid, 1954). Nitrates, however, are denitrified by many species of microorganisms in the presence of food, if oxygen levels are low. The oxygen in nitrates is utilized by the organisms, and the nitrogen is liberated as nitrogen gas (Johnson and Shroepfer, 1964). Nitrates can be beneficial in heavily polluted surface waters, but are detrimental in clean waters.

Denitrification by microorganisms is a useful route for ultimate disposal of nitrogen. Several schemes involving activated sludge have been proposed for denitrification. One system being studied at Pomona, Calif., uses microorganisms growing on carbon columns to denitrify water using methanol as a food source (Parkhurst, Dryden, et al., 1967).

Sulfur in waste waters occurs primarily as sulfates derived from tap water. Sulfates are not considered pollutants, except when they contribute to total dissolved solids. Moreover, sulfates cannot be removed from waters by precipitation with calcium because a saturated solution of calcium sulfate contains nearly 1300 mg./l. of sulfate.

Sulfates are reduced to sulfides in anaerobic digesters and can be precipitated by metals especially iron which forms slightly soluble ferrous sulfide. When sludge containing ferrous sulfide is burned, the sulfur is released as oxides of sulfur and may be an air pollution problem. Soluble sulfides, including ferrous sulfide, will precipitate most heavy metals except chromium, and, thus, remove them from the system. For this reason, it has been suggested that sulfates be fed to digesters to prevent poisoning by heavy metals, especially copper and zinc (Masselli, et al., 1967). Sulfides are possible precipitants for mercury, silver, arsenic, and lead as well, but liberation of the metal under oxidizing conditions must be considered.

Any form of reduced sulfur, as well as sulfate salts of ammonia and organic cations, will liberate oxides of sulfur upon incineration. Sulfur concentrations up to 2% in digested sludge, on a dry solids basis, make this fuel as bad as many grades of coal, from an air pollution point of view. One way of controlling pollution from sulfur in fuels is to supply calcium and magnesium oxides to the combustion zone (Potter, Harrington, et al., 1968). It is quite possible that lime, waste lime sludges, or even ground limestone or dolomite added to the sludge would control sulfur oxide emissions from sludge incinerators. Much will depend on the design of the incinerator. Furnaces for burning the black liquor from paper pulp production successfully control sulfur losses when burning sodium sulfide and organic matter dissolved from wood (Malc, 1967).

Adequate disposal means for soluble salts in inland areas are presently unavailable, except in locations where deep-well injection is practical (Koenig, 1964). Cations of sodium, potassium, calcium, and magnesium, in

combination with anions of chloride, bicarbonate, and sulfate, make up the principal components of total dissolved solids. The Public Health Service Drinking Water Standards of 1962 recommend not over 500 mg./l. total dissolved solids, although up to 1000 mg./l. is acceptable in some areas. Chlorides are further limited to 250 mg./l. In irrigation waters, monovalent ions, especially sodium and chloride, are more harmful than calcium, magnesium, sulfate, carbonate, and bicarbonate ions (McKee and Wolf, 1963). Only calcium and magnesium can be economically precipitated from water, and their removal ordinarily does not significantly improve the level of total dissolved solids. The extreme dilution of the soluble salts makes their recovery for use as raw materials uneconomical (Christensen, McIlhenney, et al., 1967). Because they are pollutants, the uncontrolled discharge of brines to unlined surface pits is prohibited in some states. In many arid areas, it is possible to evaporate brines to dryness in properly lined solar evaporation ponds. This, at least, reduces the cost of transporting brines to the ocean or of storing the solids in sealed cavities.

The only acceptable sites for disposal of salts in solution are the ocean or salt lakes. In some areas, salt brines collected in lagoons are discharged to the river during a spring flood. Properly controlled, salts in limited quantities might not pollute some rivers at high flow.

Residual flows from such advanced waste treatment processes as reverse osmosis, electrodialysis, ion exchange, or distillation ordinarily are not concentrated more than tenfold, and contain 5000 to 15,000 mg./l. TDS. This is still much more dilute than sea water, which contains 35,000 mg./l. TDS. Higher TDS concentration precipitates scale on the membranes or heat transfer surfaces (Neale, 1964). Calcium carbonate deposits first, followed by calcium phosphate. Scale from these salts can be controlled by the addition of sufficient acid to neutralize the alkalinity or by prior lime treatment of the water. The next scale to deposit is usually a form of calcium sulfate. These precipitates form slowly and may continue to form scale for days. Magnesium chloride hydrolyzes in hot water to form insoluble magnesium oxychloride, liberating HCl.

Scale formation and slow equilibrium of precipitates cause minimal trouble in solar evaporation ponds. Fortunately, many water-short inland areas, where desalting techniques will be required, also are arid areas with low cost land where solar evaporation ponds can be used. Submerged combustion evaporates water without involving any solid heat transfer surfaces, and may be useful where solar evaporation is impractical (Cronan, 1956). Scaling problems need not be insuperable, even for high-efficiency, multiple-effect, evaporators. Again, the experience in the pulping industry shows that salt solutions containing organic material can be concentrated to 50% solids on a continuous basis.

Ion exchange

The hardness-forming ions, calcium and magnesium, can be removed as calcium carbonate and magnesium hydroxide. There may be a market for magnesium oxide from magnesium hydroxide in some cases, but it will probably be more economical to recover magnesium from raw water before it enters the municipal distribution system. Ion exchange resins and zeolites used to remove hardness from water are regenerated with an excess of brine or with a combination of acidic and basic regenerants. The latter contains calcium and magnesium chlorides and excess sodium chloride. Some areas prohibit disposal of this waste salt solution to surface or ground waters.

Borates in sewage originate from cleaning compounds, especially the perborates used in solid bleaches. Borates are not very toxic to animals and microorganisms, and present no problem in drinking water. However, many agricultural crops, especially fruit trees, can be poisoned by less than 1 mg./l. of boron (McKee and Wolf, 1963). Currently, there is no satisfactory method for removing borates from irrigation water. Borates stay with the dissolved salts in desalting processes. Ion exchange resins with selectivity for borates have been claimed but their efficiency and useful life are unknown. The regenerant brine from such a resin would contain the borates in solution and would have to be disposed of as a salt brine.

Trace elements may occur in municipal waste waters as a result of spillage, corrosion, and additives to some cleaning and processing compounds. Many metals form insoluble hydroxides or carbonates. Calcium, magnesium, strontium, barium, aluminum, trivalent chromium, manganese, iron, cobalt, nickel, and copper can be removed by lime clarification. Lime precipitate may also remove zinc, cadmium, mercury, arsenic, tin, antimony, and lead by adsorption. Sulfides, as already noted, precipitate heavy metals, and septicity in sewers may reduce pollution by removing mercury, zinc, and copper ions from the sewage. Some metals—notably mercury, cadmium, and zinc—are strongly adsorbed on organic matter and are collected in primary or secondary sludges (McDermott, Barth, et al., 1963). Oxidation may liberate these metals, producing toxic flue gases or poisoning solids. Chromates in municipal waste waters may come from electroplating rinse waters, tanning wastes, or from cooling tower water. Removal of hexavalent chromates is difficult (Gursham, 1963). Chromates can be reduced with sulfur dioxide or under anaerobic conditions to trivalent chromic salts which form insoluble carbonate and hydroxide precipitates.

Cyanides are also found in electroplating wastes. Because they are highly toxic, strong controls on their disposal are required. The most common disposal method for cyanides is oxidation by chlorine to cyanates which hydrolyze to urea (Gursham, 1963). Selenium occurs in some surface waters and may get into sewage from industrial spills. There is no satisfactory way to remove selenium from waste waters. Heavy metals, cyanides, selenium, and arsenic all are so toxic and difficult to deal with in dilute solution that they should be controlled at the source and not permitted to enter municipal sewers.

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